



Environmental Effects of Dredging Technical Notes



Organic Matter Quality and Partitioning of Polychlorinated Biphenyls

Purpose

This technical note reports the initial results of laboratory testing conducted to examine the partitioning of polychlorinated biphenyls (PCBs) to organic carbon of differing degrees of aromaticity.

Background

Over the past 10 years, the U.S. Environmental Protection Agency (EPA) has pursued development of single-chemical sediment quality criteria (SQC). Equilibrium partitioning of neutral organic chemicals between the organic carbon fraction of bedded sediments and the interstitial water of the sediments provides the theoretical basis for the most popular approach to development of SQC. The solution phase of the chemical in equilibrium with the sediment is considered to represent the bioavailable fraction and to enable the conversion of existing water quality criteria (WQC) into SQC or sediment quality standards.

In this approach, sediment total organic carbon (TOC) is considered to be the primary sediment phase accounting for sorption of neutral organic chemicals, and concentrations of these chemicals are therefore normalized to the TOC fraction. A chemical-unique partition coefficient (K_{OC}), applied to the TOC-normalized chemical concentration, is used to estimate the solution-phase concentration for calculation of the bioavailable fraction, which is then compared with WQC. Criteria documents for the pesticides endrin and dieldrin, and for several polynuclear aromatic hydrocarbons, have been released by the EPA for public review and may soon be promulgated.

The promulgation of SQCs with the intent that they be used as standards will result in confounding of effects-based testing procedures as they are now practiced in dredged sediment regulation under the Ocean Dumping Act and

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the Clean Water Act (Wright, Engler, and Miller 1992; Wright and Wilson 1995). Under such circumstances, it is imperative that the accuracy of the SQC estimations and the degree of uncertainty surrounding them be clearly understood.

The Corps of Engineers is presently investigating the link between contaminant levels in sediment and sediment geochemistry, as well as the utility of equilibrium partitioning approaches for predicting toxicity. In the equilibrium partitioning approach, toxicity is assumed to be related to pore water concentrations of contaminants.

The study reported in this technical note compared measured values of K_{OC} for organic matter isolated from sediment with determinations of the degree of aromaticity in sediment organic carbon.

Additional Information

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Introduction

Concentrations of truly dissolved organic contaminants in sediment pore water are regarded as the contaminant fraction available for organism uptake (Landrum and others 1985; Kukkonen, McCarthy, and Oikari 1990). The nature of sediment organic carbon can potentially affect partitioning of nonpolar organic contaminants. Evidence suggests that K_{OC} values increase as the aromaticity of sediment organic matter increases (Garbarini and Lion 1986; Chiou and others 1987; Gauthier, Seitz, and Grant 1987; Grathwohl 1990; Murphy, Zachara, and Smith 1990; Zhou, Rowland, and Mantoura 1995). However, Davis (1993) observed a nonlinear relationship between K_{DOC} (partition coefficient normalized to colloidal plus dissolved organic carbon, DOC) and the fraction of aromatic carbon for humic acids extracted from Florida soils and waters.

Kile and others (1995) reported that the K_{OC} values for carbon tetrachloride and 1,2-dichlorobenzene were relatively invariant for both bed sediments and soils, with the values of bed sediments averaging about twice those of soils. However, Kile and others (1995) also reported much higher values of K_{OC} for sediments impacted by anthropogenic contamination than for pristine sediments. Dredged sediments, by virtue of their location, are almost always subject to anthropogenic inputs.

The K_{OC} values for a particular compound have been reported to vary widely between sediments (Schrapp and Oppenhuizen 1989; Brannon and others 1993,

1995a). Similar wide variations in K_{DOC} for sediment pore waters from different sediments have been observed (Chin and Gschwend 1992; Brannon and others 1995b). These results imply that partitioning of nonpolar organic contaminants to sediments is much more complex than assumed in the SQC model.

If organic matter quality differs between sediments and the differences affect partitioning, then many of the assumptions used in modeling interactions between nonpolar organic contaminants in sediment and pore waters in aquatic systems are invalid. This study was conducted to examine the changes in aromaticity of organic carbon in sediments and the effects of organic matter aromaticity on partitioning of PCBs.

Materials and Methods

Humic acids were isolated from sediments used in the study of McFarland and others (1996) or planned for later use by the methods of Davis (1993). Isolation procedures included extraction with sodium hydroxide, precipitation, and cleanup of the humic acids. Isolated humic acids were prepared for Fourier Transform Infrared (FTIR) analysis by dissolving the isolated humic substances (approximately 10 mg/ml) into a solution containing a fixed amount of potassium thiocyanate (KSCN) (1.97 mg/ml) at pH 4.0 in distilled deionized water. The KSCN served as an internal standard to normalize the adsorption in the 1,600 to 1,650 cm^{-1} region, where adsorption results mainly from the aromatic carbon content of the humic substances investigated. The internal standard facilitates quantitative comparison of peak intensities between different humic sources. This allows FTIR spectra of humic substances to be used for semiquantitative comparisons of different humic sources.

Where sufficient humic material remained after determination of relative aromatic peak heights (FP-0.331, BL-0.963, NY-0.055, and NY-1.28), the humic acid was dissolved in water and partitioning of PCBs was determined. A commercially available Aldrich humic acid, as well as three humic acids (Orange Heights soil, Orange Heights DOC, and Pine Mountain) isolated in the same manner by Davis (1993), was also tested.

Aliquots from each dissolved humic acid were spiked with ^{14}C -labeled PCB 52 at three concentrations (0.01, 0.007, and 0.004 mg/L) in each of three replicates. Total ^{14}C -labeled PCB 52 in solution was determined by liquid scintillation-counting 1 ml of the original solution. The remainder was then centrifuged for 1 hr at $7,400 \times g$. A 2-ml aliquot of the centrifugate was then passed through a C-18 Sep-Pak, and a 1-ml aliquot of the eluant was counted to determine the concentration of PCB 52 bound to DOC (Landrum and others 1984). Truly dissolved PCB 52 was determined as the difference between the total counts in the original solution and the counts following passage through the C-18 Sep-Pak. Truly dissolved PCB 52 is that not associated with dissolved or colloidal humic acid.

The DOC content of the humic acids in distilled water was determined using an Astro Total Organic Carbon Analyzer model 2100. The DOC was used to calculate the K_{DOC} .

Results and Discussion

The internal standard normalized FTIR peak heights of the humic substances investigated indicated that there are significant differences in the aromatic character of the materials (Table 1). The relative peak height for the Aldrich humic acid was similar to the value (1.03) determined by Davis (1993). Of the materials isolated and characterized in this study, FP-0.331 had the highest peak height ratio for humic substance aromatic carbon functional groups. The relative aromatic peak heights of the humics isolated by Davis (1993) ranged from 0.39 to 0.95, compared with the range of 2.21 to 5.76 for the humics isolated from sediments. The materials isolated in this study showed higher relative content of aromatic carbon than either the Aldrich humic acid or the humics isolated and characterized by Davis (1993).

| Table 1. Peak Height Ratios for Humic Substance Aromatic Carbon (1,600 cm⁻¹) Functional Groups | | |
|--|------------------------------|--|
| Humic Acid Source | Sediment TOC, percent | Peak Height Ratio (1,600 cm⁻¹) |
| Aldrich humic acid | NA ¹ | 0.90 |
| Orange Heights DOC | NA | 0.57 ² |
| Orange Heights soil | NA | 0.60 ² |
| Pine Mountain | NA | 0.39 ² |
| FP-0.331 | 0.331 | 5.76 |
| NY-0.055 | 0.055 | 3.23 |
| BL-0.963 | 0.963 | 2.70 |
| NY-1.28 | 1.280 | 2.21 |
| Note: Peak heights are normalized to the response of the internal standard (KSCN) at 2,050 cm ⁻¹ and are in units of milligrams KSCN/milligram humic C. | | |
| ¹ Not available. | | |
| ² Data from Davis (1993). | | |

The largest differences were between the materials from soils and river water isolated by Davis (1993) and the sediment humics isolated in this study. This suggests that sediments may be more aromatic in character than humics isolated from soils and water. This may be the reason that Kile and others (1995) found that sediments have K_{OC} values for nonpolar organic contaminants twice those of soils.

McFarland and others (1996) concluded that bioavailability of PCB 52 was highly variable and not linear with sediment organic carbon content at low TOC levels. One reason for these findings may have been the differences in relative aromatic peak height of the humic acids isolated from the sediments. The total organic carbon content of the sediments was not related to the relative degree

of aromaticity of these sediments. For example, NY-0.055 (containing 0.055 percent TOC) showed a higher peak height ratio for humic substance aromatic carbon functional groups than did BL-0.963 and NY-1.28. Both these sediments contained higher levels of TOC, but were lower in peak height ratios for humic substance aromatic carbon (Table 1). These results suggest that the aromatic character of TOC may explain many of the contradictions noted in investigations of sediments involving partitioning of nonpolar organic contaminants to sediment organic matter.

Partitioning, or distribution of a hydrophobic organic compound between dissolved organic carbon and water at equilibrium, is mathematically described as follows:

$$K_{DOC} = C_{DOC}/C_w$$

where

K_{DOC} = distribution coefficient, L/kg

C_{DOC} = concentration of contaminant sorbed to the dissolved organic carbon, mg/kg

C_w = truly dissolved aqueous phase PCB 52 concentration, mg/L

Values of K_{DOC} were computed by regression of sorbed (normalized to DOC concentrations) versus truly dissolved PCB. Slopes, standard error of the slope, y-intercepts, and regression coefficients (r^2) are also presented in Table 2. Error in estimates of the slopes averaged 33 percent for all humic acid solutions. Error included differences between replicates and experimental procedure. Regression coefficients ranged from 0.44 to 0.90.

| Table 2. Coefficients for Regression (n = 9) of Truly Dissolved and Bound PCBs in DOC | | | | |
|--|--------------|--------------------------------|------------------|-------------------------|
| Humic Acid Source | Slope | Standard Error of Slope | Intercept | r^2 |
| Aldrich humic acid | 5,604 | 2,537 | 4.82 | 0.49 |
| Orange Heights DOC | 6,194 | 918 | -5.4 | 0.90 |
| Orange Heights soil | 5,682 | 1,642 | -0.12 | 0.66 |
| Pine Mountain | 50,934 | 19,020 | 68.34 | 0.51 |
| FP-0.331 | 80,305 | 52,664 | 137 | 0.44 |
| NY-0.055 | 73,426 | 10,471 | -74.3 | 0.88 |
| BL-0.963 | 22,600 | 5,410 | 31.8 | 0.85 |
| NY-1.28 | 19,982 | 6,800 | 3.07 | 0.63 |

K_{DOC} values for PCB 52 varied from 5,604 to 80,305 L/kg. PCB 52 partitioning to materials isolated and characterized by Davis (1993) was generally lower than partitioning to humic material isolated from sediment, with the exception of the Pine Mountain material. However, Davis (1993) observed that the Pine Mountain material behaved in an anomalous manner

during partitioning studies. Comparison of the K_{DOC} values measured during this study with projected values derived from the data of Davis (1993), who related K_{DOC} to log solubility for a series of PCBs other than PCB 52, showed good agreement except for the Pine Mountain humic material. The Pine Mountain projected value of log K_{DOC} was much lower (3.2) than the measured value in this study (4.71). Therefore, because of the anomalous behavior previously reported for the Pine Mountain material (Davis 1993) and the divergence in partitioning behavior of this material from that projected by the results of Davis (1993), K_{DOC} values for Pine Mountain material measured in this study were not used.

Estimated values of K_{DOC} were computed by substituting K_{OW} or log K_{OW} (octanol/water partition coefficient) for PCB 52 into the equation $K_{OC} = 0.411K_{OW}$ (Karickhoff 1981) or $\log_{10} K_{OC} = 0.00028 + 0.983 \log_{10} K_{OW}$ (DiToro and others 1991), respectively. The value of log $K_{OW} = 5.84$ for PCB 52 was obtained from Hawker and Connell (1988). The measured values of K_{DOC} were consistently lower than the estimated K_{DOC} value (5.74), calculated using the method of DiToro and others (1991). The method of Karickhoff (1981) also somewhat overestimated measured values of K_{DOC} (5.45).

Measured values of K_{DOC} in humic materials extracted from soils, water, and sediment were not constant and were consistently lower than the value estimated by the method of DiToro and others (1991) or Karickhoff (1981). However, a strong linear relationship ($r^2 = 0.85$) existed between measured log K_{DOC} values of PCB 52 and the FTIR peak height ratios for humic substance aromatic carbon functional groups (Figure 1). These results demonstrate that the quality of organic carbon strongly affected K_{DOC} values of PCB 52. This relationship indicates that differences between measured K_{DOC} values can be caused by variations in the composition of natural organic matter, specifically variations in the aromaticity of TOC, as postulated by others (Gauthier, Seitz, and Grant 1987; Grathwohl 1990; Davis 1993).

Results indicate that the relative degree of aromaticity in sediments is not constant and differs markedly from that measured in humic acids isolated from soils and river waters. Equilibrium partitioning models that are used to predict concentrations of nonpolar organic contaminants in sediment pore water and which assume that all organic carbon is equal in sorptive capacity are making an erroneous assumption.

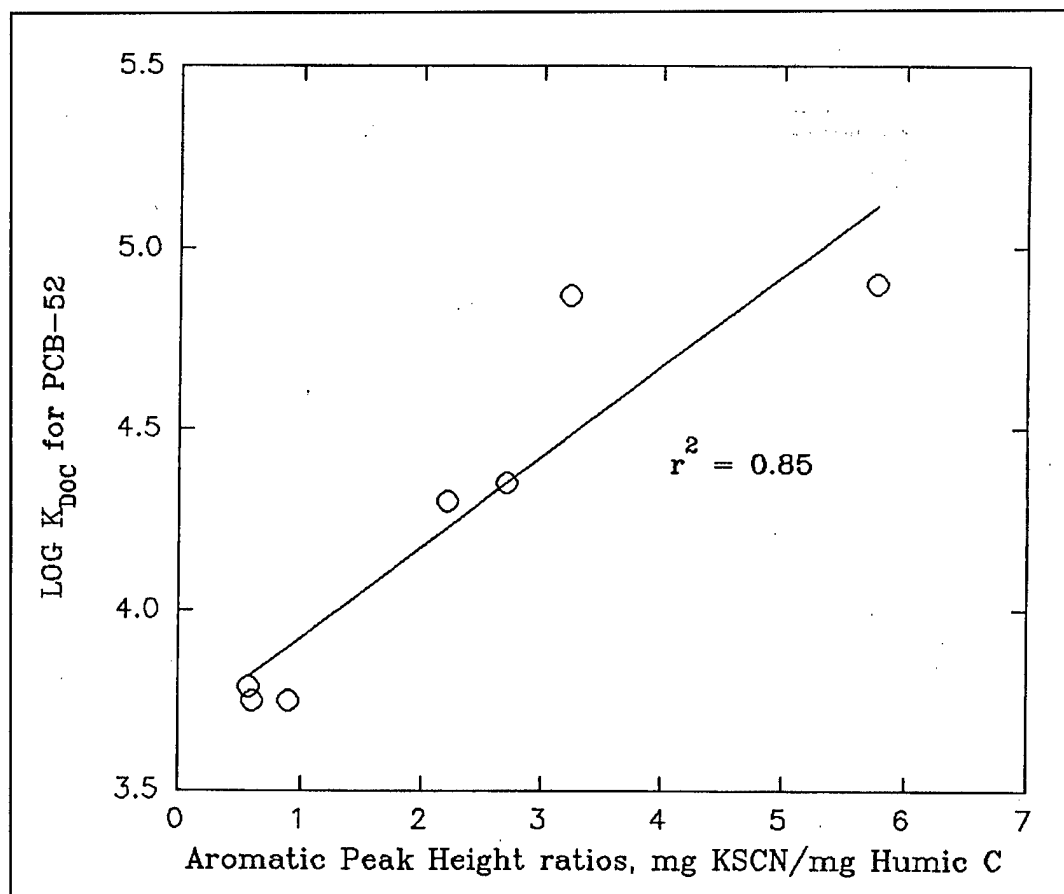


Figure 1. Plot of $\log K_{DOC}$ for PCB-52 versus aromatic peak height ratios for extracted humic materials

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